

## A Method for Studying Precombustion Reactions of Liquid Propellants

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### Introduction

Since their inception, rocket engine development programs have been plagued with sporadic explosions. Some of these have occurred on start, others during a run, and still others on shutdown. Ordinarily, design changes are relied upon to correct such situations. A more fundamental approach was considered at Bell which consisted of looking at the chemistry of the system.

All work done along this line was based on the hypothesis that liquid phase reactions occur between rocket propellants and exert an influence on subsequent combustion reactions. In the case of nitric acid-hydrocarbon engines, e.g., liquid phase oxidation and/or nitration reactions appear possible. Depending on which reaction occurs or predominates, one can anticipate smooth or troublesome combustion.

Testing this hypothesis began with a literature survey which yielded little conclusive evidence. This led to a step-by-step experimental approach to rocket operating conditions of temperature, pressure and reaction time, and produced a useful method for studying precombustion reactions of liquid propellants.

### Summary

The heart of the method was an apparatus designed to bring propellants separately to conditions of temperature and pressure equivalent to those encountered on injection into an operating rocket engine. The propellants were next flowed into the arms of a "Y" Tube, allowed to react in the stem, then subjected to a chemical stop. Reaction time was controlled by flow-rate and stem dimensions. In its final form this apparatus brought together propellants preheated to 300°F at 575 psig, allowed them to react for 15 milliseconds, and delivered the products in solutions suitable for conventional analyses. These analyses, largely spectrophotometric, showed to what extent particular reactions had occurred. Reaction mechanism was elucidated by analyses of products from parallel mixing experiments carried out under less drastic conditions and allowed to go to completion. The following is an account of the evolution of this apparatus and its role in the overall method.

### Technical Approach

Experimental work began by mixing small quantities of typical propellants, WFNA (White Fuming Nitric Acid) and JP-4, in various proportions in the hope that at certain mixture ratios solutions would form which could be analyzed for oxidation products or explosives. Since little direction was afforded by the literature, initial mixing was done in open beakers without impressed heating. Exothermic reactions took place without incident in every case but no solutions resulted. Mixture ratio variation was achieved by dropwise addition of JP-4 in increments up to 15g. to 15g. of WFNA and vice versa.

To preserve all reaction products for analysis, the experiments were repeated using a two-neck flask fitted with a reflux condenser and thermometer. The set-up was contained in a water bath sitting on a magnetic stirrer capable of mixing the water and propellants. In these experiments heating was continued until reaction had ceased as evidenced by the cessation of nitrogen dioxide evolution. Temperature-time profiles were taken and the resulting mixtures were set aside for observation and analyses. Some showed a distinct third liquid phase assumed to be a collection of reaction products or the beginnings of solution formation.

At this point, mixing conditions were made more drastic in the hope of forcing solution formation. A three-neck flask was adopted and a high speed stirrer (1400 rpm) introduced. The flask was stationed on a hot plate. By this time analytical work had shown that the most interesting results were occurring at mixture ratios of  $O/F = 0.3, 1.0, 2.0, 4.0$  and  $5.0$  so all future work was centered about these values. The procedure was much as before except that mixing time was varied within definite limits maintained by transferring the flask to an ice bath at the appropriate time. An extension of this work involved a series of high speed mixing studies carried out under the influence of intense light and/or sound. For these experiments the mixing flask was mounted in a box fitted with a lens which directed ultraviolet radiation of rocket engine intensity on the propellants. This reaction was from a filtered carbon arc. Rocket engine sound was simulated by directing a recording of a rocket engine run at an intensity of 122 decibels at the flask. Again no solutions formed but analyses of the individual phases from these and earlier experiments pointed to the direction for future work.

Careful observation disclosed that at least two liquid phases existed even during high speed mixing at reflux temperature. In many cases a third liquid phase was present and in some instances solid phases appeared. The liquid phases were easily distinguished in that they formed layers, the top being pale yellow and the bottom orange. Where a third phase appeared it was seen as a yellow band of liquid between the other two layers. One type of solid phase appeared in the middle layer, another in the lower layer. Using conventional techniques the liquid and solid phases were isolated and submitted for analyses.

It quickly became apparent that the top layers were largely unreacted fuel, the bottom unreacted oxidizer, and the middle reaction products. The crystals in the middle layers were identified as a p-nitrobenzoic acid and those in the bottom layers were oxalic acid. Attempts at further characterization by organic analytical techniques proved futile primarily because of the number of constituents in JP-4. Accordingly, it was decided to rely on experiments with pure hydrocarbons to elucidate the nitration and oxidation reaction sequences obviously in operation. At the same time data from spectrophotometric analyses focused attention on the need for studies under more vigorous conditions and at shorter reaction times.

The spectral approach was to dilute samples of each phase as required with an appropriate solvent, e.g., 2-propanol and measure absorbance as a function of wavelength in the ultraviolet region of the spectrum. A persistent peak occurred at 260 m $\mu$  in a curve remarkably similar to ones for nitroaromatics. As indicated earlier, this was quite obvious for mixtures prepared at  $O/F = 0.3$ . A plot of all the data at this wavelength for this mixture ratio gave three curves of absorbance vs time corresponding to the top, middle and bottom layers respectively. Extrapolation of these curves back to "0" time showed that significant reaction must have taken place in less than a minute. Extrapolation to "0" time was possible by assigning the absorbance of JP-4 to the upper phase, the absorbance of WFNA to the lower phase, and a value of zero for the middle phase. The fact that absorbances for the middle and lower phases were on the wane beyond the earliest measured time of approximately one minute showed reactions had occurred prior to this point. Subsequent studies explained the decreases in absorbance with time on the basis of interference from products produced by competing oxidation reactions.

The first attempt to reduce reaction time from minutes to milliseconds was made with a crude, manually operated "Y" Tube apparatus. The principle behind such an apparatus is relatively simple. One propellant is flowed at a controlled rate into one arm of the "Y", the other propellant into the second arm. Depending on the flow-rates chosen the propellants mix at a certain mixture ratio and react in the stem. Reaction time is then a function of total flow-rate, cross sectional stem area and effective stem length, i.e., the distance over which reaction is allowed to proceed. The apparatus built to reduce this principle to practice is described as follows.

Two steel tanks fitted with provisions for pressurization were connected to the arms of a metal "Y" Tube having an I.D. of 0.4 cm. In the oxidizer arm was installed an orifice of 1mm and in the fuel arm an orifice of 2mm. Upstream of each orifice was a quick-opening hand valve. Propellants loaded into the tanks and flowed out under 15 psig on the oxidizer side and 20 psig on the fuel side mixed in the stem at an O/F ratio of 0.3 and ejected from the stem at an overall flow-rate of 44 cc/sec. These values were established by flowing methylene chloride (in place of acid) and JP-4 through the system separately to establish mixture ratio and collectively to establish total flow-rate. Methylene chloride has the same density as WFNA and was used during calibrations for safety considerations. The next item has to do with control over effective stem length.

Originally, it was planned to use a "Y" Tube with a transparent stem and monitor reactions by direct spectral analyses at various stations down the stem to provide a record of reaction vs time. Unfortunately, absorbance was too high so a chemical stop was adopted. This consisted of a rapidly stirred, cold solution of equal parts of methylene chloride and n-heptane. Preliminary experiments indicated that such a solution not only quenched reaction but gave the products in form suitable for spectral analysis at a convenient time and location. This approach compounded design problems, though, in demanding a method for isolating a relatively small, representative sample.

This problem was solved by putting a cover with a hole in it on the beaker of quench solution. To the cover was welded a tube with holes overlapping the one in the cover. Into this tube was fitted a second, similarly perforated tube connected to a hydraulic actuator. Steady movement of this tube brought all holes in line momentarily and allowed a definite amount of material to enter the quench solution. Travel was adjusted during runs with methylene chloride and JP-4 to trap 14cc. The balance of the propellant was discarded.

Runs were made with live propellant after the effective stem length was adjusted to 15cm. This is the distance from the intersection of the "Y" to the surface of the quench solution. Under these conditions, reaction time was limited to 43 milliseconds. Following the run, the quench solution was diluted to a given volume and examined spectrophotometrically. Absorbance about 260  $\mu$  was compared with a blank and with that obtained from a composite curve for a corresponding high speed mixing reaction which had been allowed to go to completion. These data showed that about 1/3 as much nitroaromatic forms in 43 milliseconds as in 30 minutes.

Having demonstrated a point, attention was next turned to refining the apparatus for work at higher temperatures and pressures. For safety sake, operation was made remote by replacing the hand valves with a solenoid operated, bi-propellant valve. To increase flexibility, the welded "Y" was replaced with a block drilled to form the channels for the "Y" and tapped to allow insertion of stems of various lengths via standard fittings. To provide better control over flow-rate, vane-type flowmeters were installed. The flowmeters were checked out by flowing a mixture of trichloroethylene and acetone through the system, collecting fractions in given lengths of time and measuring their refractive indices. Mixture ratio was established from a calibration curve and on comparison with flowmeter data showed excellent agreement. To provide better sampling, a shutter-type sampler was built.

The new sampler consisted on a piston-driven shutter programmed to momentarily expose a hole in a perforated, beaker cover. Programming was effected by loading the piston spring to 40 psig with nitrogen gas, then adjusting a bleed valve until 10cc portions of trichloroethylene/acetone mixtures were trapped.

Use of this equipment with two different stem lengths corresponding to 40 and 20 milliseconds of reaction time respectively gave data proving that quench was instantaneous and significant reaction was taking place within 20 milliseconds.

The same results were obtained after installing a back pressure orifice in the stem of the "Y" Tube. This was done in preparation for tests at elevated temperatures. By use of back pressure, reaction in the stem would be restricted to the liquid phase even if the propellants rose above their normal boiling points. Glas-Col heaters were attached to the tanks to allow prerun warm-up.

Satisfactory runs were made in this configuration over the temperature range 75 to 150°F. As anticipated, nitration reactions increased with temperature as shown by an increase in absorbance in the 260 mμ region of the spectrum. Attempts run at temperatures above 150°F were thwarted by a number of problems.

Corrosion of the steel tank by hot acid contaminated the oxidizer with salts and drastically reduced the concentration of the acid. The corrosion problem was solved by using WFNA modified with a corrosion inhibitor. The inhibited acid, called IWFNA, contained approximately 0.5 wgt% hydrofluoric acid.

Uncertainties in temperature due to heat loss in the flow system were solved by installing thermocouples in the arms of the "Y" Tube. The output from the fuel arm was fed to a temperature recorder. The output from the oxidizer arm was fed to an electronic device wired to activate the sampler on attainment of a predetermined temperature.

Reruns over the temperature range 75 to 150°F gave data equivalent to that obtained with WFNA. No corrosion was encountered above 150°F but thermal decomposition reduced the concentration of the oxidizer. An analysis of the situation showed it took approximately two (2) hours to reach 150°F and during this time water content increased from <2% to >7% at the expense of nitric acid concentration. Decomposition was reduced by strapping Calrod heaters to the tanks and covering them with insulation. This reduced heating time from hours to minutes. In addition, the tanks were prepressurized above the anticipated vapor pressure of the propellant on cessation of heating. With these modifications, a temperature of 200°F was reached with an attendant increase in nitration.

Above 200°F, the flowmeters bound and gave erratic data. The trouble was traced to the Kel-F shaft bearings. Reliability was re-established by replacing the flowmeters with differential pressure gages. These were strain-gage pressure pick-ups installed on either side of the line orifices. Calibration was accomplished by running the differential pressure gages in series with the vane-flowmeters to approximately 200°F.

Attempts to run above 200°F were still unsuccessful though, because of increasing temperature differentials between the tanks and "Y" Tube, and a tendency for the propellants to flash-off on leaving the "Y" Tube. The temperature differential problem was solved by installing the tanks and flow system in an insulated chamber attached to a Chromolox heater. By admitting hot nitrogen to the chamber during the propellant heating cycle and monitoring the operation with a network of strategically placed thermocouples, propellants and hardware were brought to the desired temperature.

The propellant flash-off problem was solved by adding an extension, dubbed a Jet Mixer, to the "Y" Tube stem. This extension, which brought the propellants

outside the insulated chamber, was so designed as to take a stream of cold quench solution from an independent cooling and circulating system and inject it into the issuing propellant stream. The flow-rate of quench solution was determined by prior calibration and the sampler was modified slightly to handle a larger volume of liquid.

In this final form the apparatus was used for runs to 300°F with propellants pressurized up to 575 psig, conditions simulating those of injection into an operating rocket engine. Although there were minor variations, mixture ratio was approximately 0.3 O/F for these runs and reaction time was approximately 20 milliseconds. Again nitration reactions increased with temperature over the entire range studied.

Figure 1 is a schematic for the "Y" Tube apparatus. Figure 2 shows the increase in reaction absorption with increase in temperature over the range 75 to 300°F.

Parallel with this work, high speed mixing studies were conducted with pure hydrocarbons of the principal types found in JP-4, viz., paraffins, olefins and aromatics. The compounds chosen were: n-heptane, n-heptene-2 and toluene, all of which contain seven (7) carbons. Through systematic separations, qualitative organic and ultraviolet spectrophotometric analyses, sufficient products were identified to allow postulation of probable reaction sequences. Among the products were acetic acid, oxalic acid, nitroheptene-2, 2-4 dinitrotoluene and p-nitrobenzoic acid.

With heptane, virtually no reaction takes place. (Hence the validity of its use in the quench solution). With heptene, the first reaction is replacement of an olefinic hydrogen with a nitrate group. This is followed by a sequence of oxidation and nitration reactions leading to oxalic acid. Nitration also appears to be the initial reaction with toluene. This occurs in the ring and is followed by oxidation of the chain and further nitration of the ring.

### Conclusion

Thus we have shown that liquid phase reactions can occur under rocket engine operating conditions. Further we showed a mechanism for these reactions and indicated how nitration could well get out of hand and lead to combustion instability.

More important we showed the evolution of an apparatus which in its final form is suited for kinetic studies of reactive materials under extreme conditions of temperature and pressure.

But most of all we have demonstrated an approach to a problem which features interaction of the various branches of chemistry and engineering to reach a common goal.

"Y" TUBE SCHEMATIC  
FIGURE 1

